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Optical texture of hydrochar from maize silage and maize silage digestate

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ABSTRACT

Hydrochar is a promising solid fuel produced from hydrothermal carbonization (HTC) of wet biomass feedstocks. Raw maize silage and corresponding hydrochars from 230 and 250 °C, and maize silage digestate and corresponding hydrochar from 230 °C were analyzed in this study. Optical microscopy has been used to follow the transformations occurring in the hydrochars. The terms biocharospheres and biocharoplast have been proposed to describe the spherical carbonaceous material formed from the cell-walls and the molten homogeneous shapeless material, respectively, generated from biomass during hydrothermal carbonization. Hydrochar produced from digestate under mild HTC condition had a granular structure indicating an acceleration of the nucleation with the formation of submicrometer size spheres. The reflectance of the hydrochar increased with increasing carbon content and allowed the description of sample heterogeneity, which would be useful to follow the transformations under treatments of different severities.

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1. Introduction

Hydrothermal carbonization (HTC) is a promising thermochemical treatment of biomass to solid fuel and value-added chemicals. During HTC, subcritical water reacts with fibrous components of lignocellulosic biomass, and thus degrades and reconstructs them into a homogeneous, hydrophobic, and energy-dense solid known as hydrochar (Reza et al., 2014a,b). Primary reactions like hydrolysis, dehydration, decarboxylation, condensation, polymerization, and aromatization take place during HTC (Reza et al., 2014a). Hydrochar contains micro- nano-sized carbon spheres depending on the HTC process parameters such as reaction temperature, duration of reaction, and feedstock type, which make the HTC process attractive in various fields of applications, namely adsorption, soil amendment, biofuel, fuel cell, and energy storage etc. (Jin, 2014; Sevilla et al., 2011). Hydrochar could be also considered as a solid fuel, which plots in the van Krevelen diagram in the lignite region (Reza et al., 2014a,c) and can potentially replace unsustainable coal to a certain extent (Funke et al., 2013). However, production of homogeneous hydrochar from various feedstocks is challenging, and solid product (hydrochar) is typically characterized by bulk techniques such as elemental and proximate analyses, which are not able to describe sample heterogeneity.

Optical microscopy is one of the most versatile tools for characterization of coal and carbon-rich materials. This allows a precise qualitative and quantitative estimation of the amount of isotropic (disordered structure) and anisotropic (ordered stacked domains of different sizes) optical textures of a solid fuel. In addition, domain size, which can also be distinguished by optical microscopy, is closely related to the reactivity of the material, as edge carbons are generally more reactive than inner carbons (Crelling and Gray, 1998; Hurt et al., 1995). The development of homogeneous energy boosted hydrochar depends on oxygen-rich volatile component and rate of crosslinking polymers in the structure of raw feedstock and hence heavily depends on HTC reaction conditions (Reza et al., 2012, 2013a,b, 2014a,b). Optical microscopy is potentially suitable to observe the structural changes of solid hydrochar during HTC. As microscopy is used to characterize coal for years, this method also enables to compare hydrochar fuel properties with coals. Thus, the main goals of this study were: (1) to study the optical texture of maize silage and maize silage digestate and corresponding hydrochars produced in different HTC conditions to follow the transformations occurring in the material, and (2) to discuss the variation of optical texture in relation to physico-chemical analyses.

2. Materials and methods

2.1. Hydrochar production

Maize silage was acquired from a locally grown test site at Leibniz Institute for Agricultural Engineering (ATB), Potsdam, Germany. Maize

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Table 1
Fiber and ultimate analysis of hydrochar from maize silage and maize silage digestate.

Sample	Mass yield[a] (%)	Ash (db[b]%)	C (daf%)	H (daf%)	N (daf%)	S (daf%)	O (daf%)	HHV[c] (MJ.Kg^{-1})	Hemicellulose[d] (%)	Cellulose[e] (%)	Lignin[f] (%)
RMS	–	6.7 ± 3.0	45.4 ± 5.2	6.7 ± 0.5	0.7 ± 0.2	0.3 ± 0.1	40.6 ± 8.0	17.4 ± 1.6	26.3 ± 2.0	32.7 ± 2.1	7.0 ± 2.4
MS Digestate	62.4 ± 5.0	11.4 ± 5.1	41.1 ± 4.5	5.4 ± 0.5	2.6 ± 0.5	0.2 ± 0.1	39.3 ± 9.5	14.3 ± 1.0	0.5 ± 0.2	25.5 ± 3.1	37.6 ± 2.1
HTC 230 MS	45.3 ± 4.5	4.7 ± 1.8	57.6 ± 5.4	5.1 ± 0.3	1.2 ± 0.5	0.6 ± 0.1	31.3 ± 6.0	21.1 ± 1.8	4.8 ± 3.1	25.2 ± 1.5	24.6 ± 1.2
HTC 250 MS	39.6 ± 3.8	2.3 ± 1.5	72.5 ± 4.5	6.1 ± 0.7	0.9 ± 0.2	0.0 ± 0.1	18.2 ± 7.0	30.0 ± 1.1	0.3 ± 0.1	4.3 ± 1.2	58.3 ± 2.5
HTC 230 MSD	49.5 ± 5.1	13.3 ± 5.0	64.9 ± 4.6	6.6 ± 1.0	0.8 ± 0.2	0.0 ± 0.1	15.2 ± 9.0	28.7 ± 1.2	0.1 ± 0.1	20.8 ± 2.1	44.2 ± 2.6

[a] Mass yield = (dry weight of hydrochar) / (dry weight of feedstock).
[b] db = dry basis; daf = dry-ash-free basis.
[c] Estimated from elemental analysis according to (Boie, 1953) and expressed in daf.
[d] Hemicellulose% = neutral detergent fiber (NDL%)–acid detergent fiber (ADF%).
[e] Cellulose% = acid detergent fiber (ADF%)– acid detergent lignin (ADL%).
[f] Pseudo-lignin% = acid detergent lignin (ADL%)–ash%.

silage digestate (MSD) was prepared by a UASS (Upflow anaerobic solid state) reactor using thermophilic condition (temperature 55 °C). The details of anaerobic digestion and UASS reactor can be found elsewhere (Pohl et al., 2012). The feedstocks' size was reduced to 5 ± 3 mm. Moisture content of raw feedstock was 13 ± 1 wt.%. For a typical HTC experiment, around 50 g of dry maize silage or dry digestate and 600 ml of DI (deionized) water were transferred into a 1 l Parr stirred reactor (series 4520, IL, USA). The experimental condition was set at either 230 or 250 °C with a reaction time of 6 h and a 3 °C min^{-1} heating rate. The reactor was stirred continuously at 90 rpm throughout the HTC. At the end of reaction period, the reactor was cooled down naturally. It took 3–4 h to cool down the reactor from 250 to 25 °C. Hydrochar was filtered (ROTH type 113 P filter) for 20 min. The solid product was dried in a heating oven overnight at 105 °C and stored in a ziplock bag for further use. In this study, terminologies RMS, HTC 230 MS, HTC 250 MS, HTC 230 MSD are used for raw maize silage, maize silage hydrochar produced at 230 °C, maize silage hydrochar produced at 250 °C, and digestate hydrochar produced at 230 °C, respectively.

2.2. Hydrochar characterization

Elemental carbon, hydrogen, nitrogen, and sulfur (CHNS) were measured using a Vario El elemental analyzer (Elementar Analysesysteme Hanau, Germany). Sulfonic acid was used in this elemental analysis as reference and two ovens were set at 1150, and 850 °C, respectively. Each sample was analyzed three times, and the oxygen content was calculated by difference (O% = 100 − (C% + H% + N% + S%) − ash%). Dry matter (DM) was determined by treating samples at 105 °C for 24 h, while ash was determined by treating DM at 550 °C for 5 h according to VDLUFA Chap. 3.5 and 8.4 (Reza et al., 2014b). The higher heating value (HHV) was calculated using the correlation of Boie and presented on a dry ash-free basis (Boie, 1953).

A modified van-Soest method using the ANKOM A200 Filter Bag Technique (FBT) was used to determine the contents of hemicellulose, cellulose, and pseudo-lignin in solid samples (Reza et al., 2013a). The solid samples were first crushed and sieved to the desired particle size (20–65 mesh) and were dried at 105 °C for 24 h prior to the analysis.

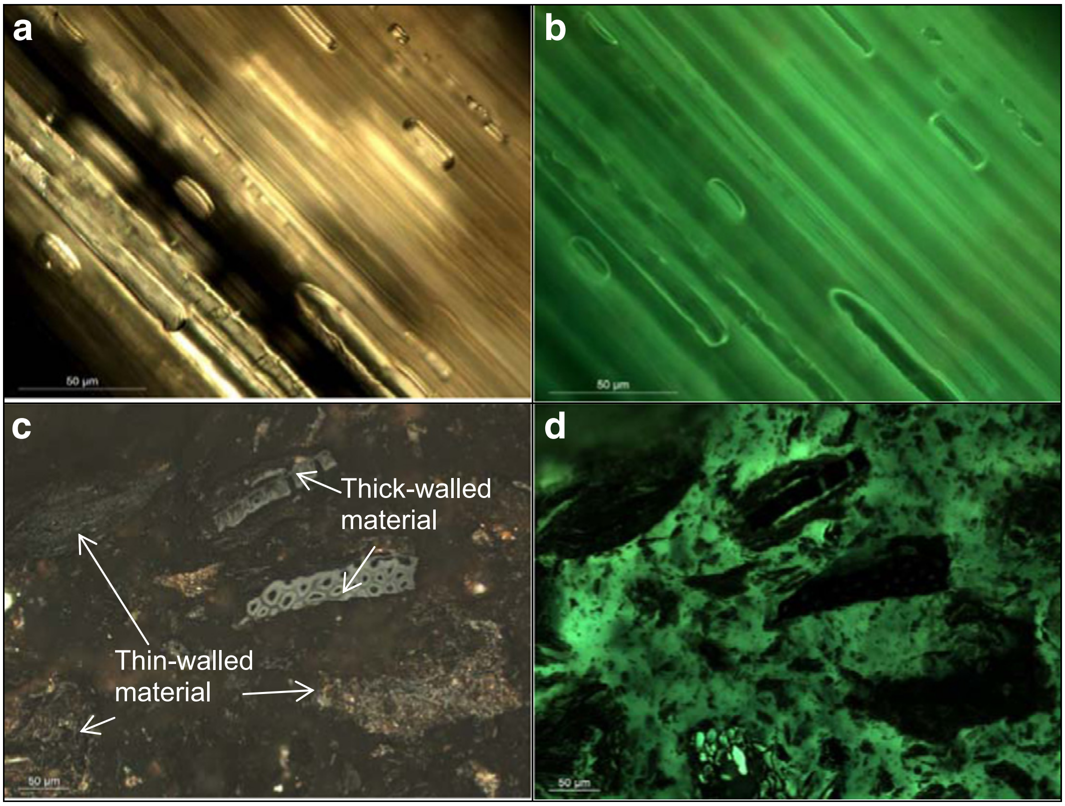

Fig. 1. Reflected light optical microscopy images of raw maize silage (RMS) and maize silage hydrothermally carbonized at 230 °C (HTC230 MS). a) RMS white light, b) RMS fluorescence light, c) HTC230 MS white light, d) HTC230 MS fluorescence light.

The contents of hemicellulose, cellulose, and pseudo-lignin were calculated from the difference of neutral detergent fiber (NDF), acid detergent fiber (ADF), acid detergent liquid (ADL), and ash as described in (Reza et al., 2014b).

For microscopic observations, solid dry hydrochars as well as their corresponding raw feedstocks had been embedded in polyester resin as typically done for coal or carbon materials (ISO 7404-2, 2009). The optical texture of embedded hydrochar was examined under a polarized reflected light microscope with oil immersion objectives. Fluorescence light was used for examining raw feedstocks and hydrochars treated at mild conditions (HTC 230 MS and HTC 230 MSD). The nomenclature used for the description of optical texture is based on that developed for coal hydrogenation residues by the International Committee for Coal and Organic Petrology (ICCP) (1993), with the necessary adaptations for application to biomass. Quantitative reflectance measurements were taken on the hydrochar material following the guidelines indicated for the measurement of vitrinite reflectance in coal (ISO 7404-5, 2009).

3. Results and discussion

3.1. Physico-chemical properties of hydrochar

Ultimate and fiber analyses along with mass yield for various hydrochars are presented in Table 1. Lower elemental carbon and higher oxygen make RMS less attractive as solid fuel as reflected by HHV values in Table 1. RMS contains relatively higher hemicellulose and ash than hydrochars and MSD. During HTC, hemicellulose and cellulose degrade with the increase of temperature, resulting to a decrease of overall mass yield. Elemental analysis points out an increase of carbon and a decrease of oxygen during HTC, which improves the

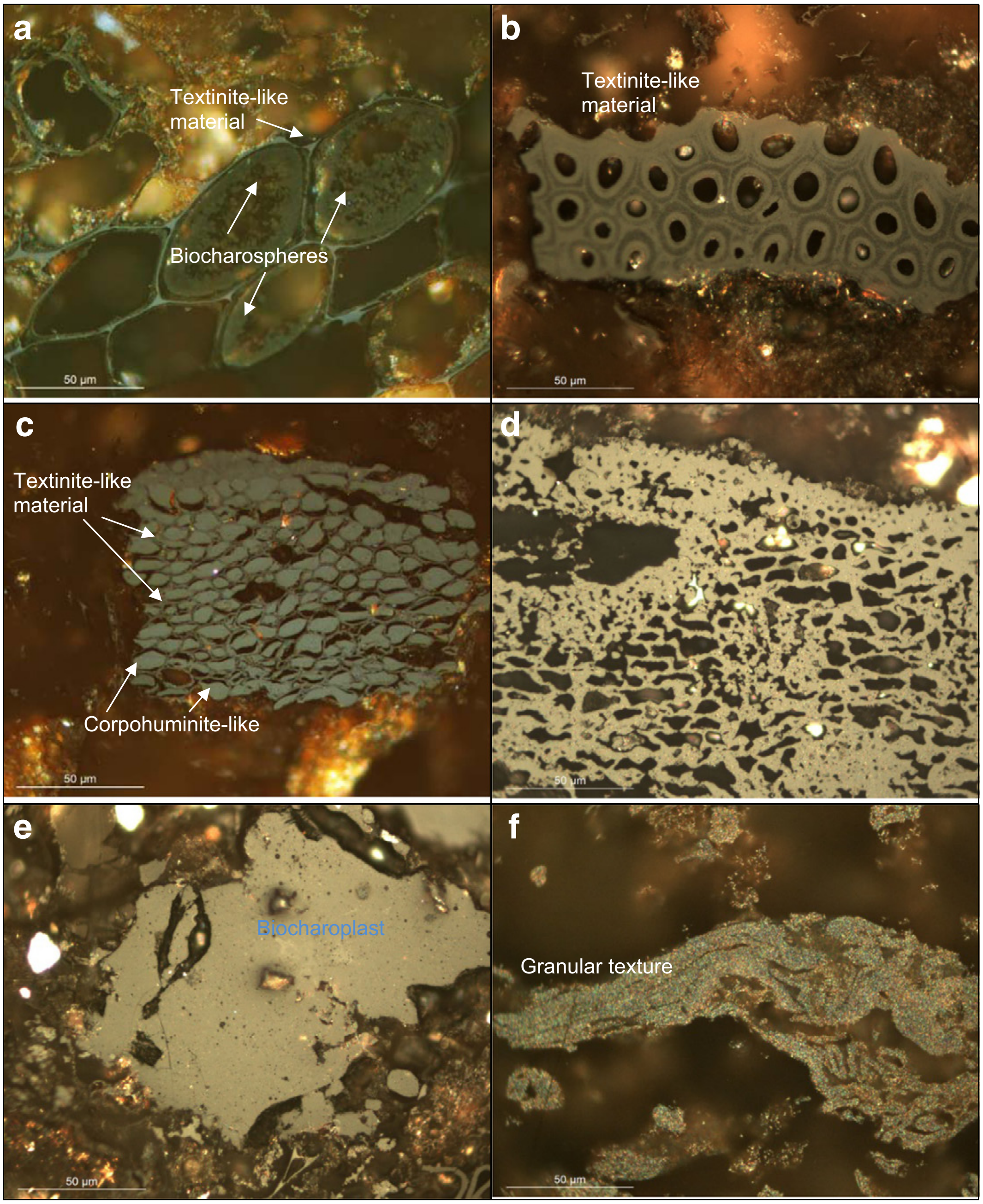

Fig. 2. Reflected light optical microscopy images of hydrochars from maize silage: a, b and c) HTC 230 MS; d and e) HTC 250 MS; f) HTC 230 MSD.

quality of hydrochar as a solid fuel. In fact, an increase of 59.7% of carbon and a decrease of 55.1% of oxygen can be observed in HTC 250 compared to raw MS from Table 1. As a result, HHV increases around 72.5% for HTC 250 MS compared to RMS. Moreover, a 20 °C increase from HTC 230 to HTC 250 was found very effective for altering fiber and elemental compositions. It has been previously reported that hemicellulose degrades around 200 °C and cellulose around 230 °C during HTC (Reza et al., 2013b, 2014a). Similar finding can be found in Table 1, as complete hemicellulose and major part of cellulose degradation can be observed in HTC 250. During HTC, crystalline fiber structures hydrolyze into various furfural and phenolic intermediates, which then undergo a series of complex reactions to form hydrochar (Reza et al., 2014a). Hydrochar has similar characteristics as acid insoluble lignin as it is insoluble in ADL (Reza et al., 2014b), and thus lignin concentration was found more than 58% in HTC 250 MS hydrochar.

The major differences between the anaerobically digested RMS and the parent maize silage are the higher ash and carbon contents and the lower amount of hemicellulose. The HTC of the MSD caused similar transformations as observed in the RMS e.g., elemental carbon, HHV, and pseudo-lignin contents increase and oxygen decreases. In fact, the lowest elemental oxygen was recorded for HTC 230 MSD in Table 1 and corresponding HHV was similar to that of HTC 250 MS. With respect to energy value, HTC 230 of MSD is adequate to get the similar energy value out of HTC 250 MS. One possible explanation for this phenomenon might be the acidity of raw MSD. One of the major steps of anaerobic digestion is the production of organic acids (mainly, acetic and formic acid) during acidogenesis, and the acidic environment remains in the digestate, which might favors HTC reactions later (Pohl et al., 2012). The microbial effects during anaerobic digestion also change the fiber structure and probably make it more amenable for HTC (Pohl et al., 2012).

3.2. Optical microscopy observations and reflectance study of hydrochar

Reflected light optical microscopy might not be the most appropriate to study RMS, as RMS is a transparent material with abundant internal reflections. However, the observations are necessary to compare hydrochars with raw feedstocks. RMS was essentially translucent and showed an intense green fluorescence, when irradiated with blue-violet light (Fig. 1a, b). Moreover, thick and thin walls were visible in the RMS, and HTC 230 MS showed cell-wall shrinkage and greater opacity compared to RMS (Fig. 1c), reflecting carbon-enrichment as observed in Table 1. Fig. 1d (HTC 230 MS) shows the complete disappearance of fluorescence. It was previously reported that hydrogenated residues of biomass (poplar wood obtained under vacuum) maintained fluorescence up to treatment temperatures of 247 °C (Kalkreuth et al., 1986). Torrefied woody biomass, heated at 250 °C for 30 min, also retained certain fluorescence properties (Pohlmann et al., 2014). These studies indicate that both reaction temperature and reaction time are relevant for the disappearance of fluorescence properties.

The internal structure of cell-walls is clearly observed (for HTC 230 MS in Fig. 2a and b) consisting of a lighter inner layer and darker outer layer as typically observed in textinite of peat and lignite (Sýkorová et al., 2005), as well as in torrefied biomass (Pohlmann et al., 2014). Occasionally rounded material associated to the tissue walls could also be observed (Fig. 2a), which has been observed in SEM (scanning electron microscopy) images, as carbonaceous microspheres formed in cellulose derived hydrochars (Sevilla et al., 2011). The term, “biocharosphere” may be introduced to name this spherical material, as it contains reference to its spherical shape and the word “char” generally indicates a carbon-rich material produced by thermal treatment. Moreover, the prefix, “bio-” refers it to biomass and makes an unequivocal distinction between this material and the hollow cenospheres generated at high heating rate from vitrinite in coal combustion or hydrogenation residues (Mitchell et al., 1977; Ng, 1983). It also allows distinguishing this material from the other carbon-rich materials generated from coal by heating in presence of oxygen depleted atmosphere such as mesophase, (typically anisotropic), or pyrolytic carbon derived from volatile condensation in carbonization processes. In addition biocharosphere could be specifically applied to the material generated during preparation of biochars or hydrochars and would not be confused with the term charosphere proposed by (Quilliam et al., 2013). The term, charosphere, is used to indicate specifically in the array of microorganisms associated to hydrochar when used for soil remediation, analogous to rhizosphere associated to plant roots. Fig. 2a illustrates the formation of dark biocharospheres close to tissue cell-walls

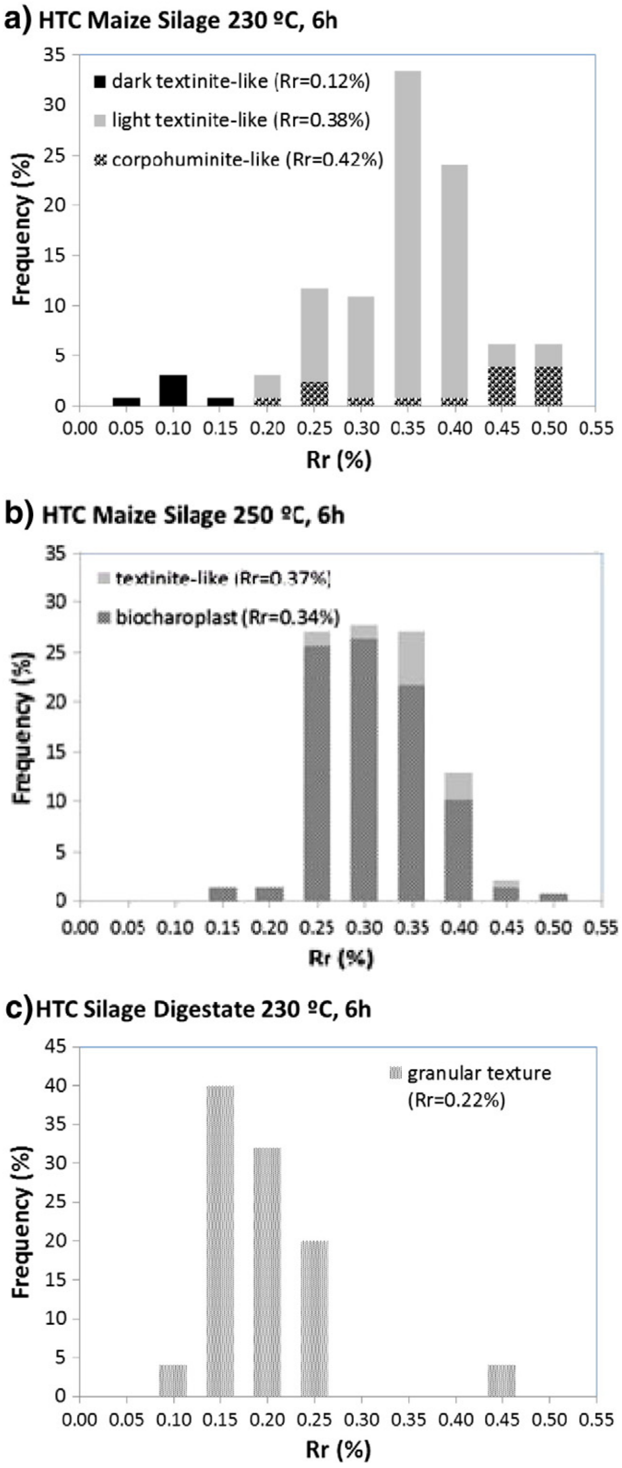

Fig. 3. Histogram reflectance of different hydrochar components. Rr = average random reflectance measured in oil.

Table 2
Random reflectance (Rr) of the measurable components in HTC samples. Note: Corpohuminite-like = cell fillings, textinite-like = cell-walls, Biocharoplast = fused structureless material. * Refers to granular structure.

Sample		Textinite-like material	Dark textinite-like material	Corpohuminite-like	Biocharoplast
HTC	Rr (%)	0.38	0.12	0.42	
230	N	106	6	17	
MS	Standard deviation	0.064	0.037	0.104	
HTC	Rr (%)	0.37			0.34
250	N	17			131
MS	Standard deviation	0.047			0.056
HTC	Rr (%)	0.22			
230	N	25			
MSD	Standard deviation	0.066			

having a similar reflectance to dark textinite. Further coalescence of the biocharospheres, if retained within the wall limits, will have the appearance of cell-fillings denoted as corpohuminite (Fig. 2c) in peat and lignites (Sýkorová et al., 2005).

The images of Fig. 2a, b and c indicate that it was not always possible to measure the reflectance of the wall-forming materials in the HTC 230 MS due to their thin walls. When possible, dark and light components of the walls were measured separately, showing a different distribution of reflectances. The biocharospheres showed similar reflectances to the darker walls supporting similar compositions for both components. The reflectance values of the dark textinite (Rr = 0.12%) were slightly lower than those recorded for torrefied biomass heated at 250 °C for 30 min (Rr = 0.15%) (Fig. 3 and Table 2) (Pohlmann et al., 2014), and also similar to those hydrogenated poplar woods prepared at 247 °C by Kalkreuth et al. (1986). However the light textinite had average values around 0.38%, close to those of the corpohuminite (0.42%), both components having similar distribution of reflectances.

In comparison, the formation of shapeless material with or without certain porosity was observed in HTC 250 MS (Fig. 2e). This material could have been formed by coalescence of biocharospheres, and collapse and homogeneization of cell-walls. It has the appearance of a molten material forming a mass with rounded borders and a relatively homogeneous, occasionally spotted surface. It also has similar appearance to isotropic metaplast formed during the plastic phase of caking coal during carbonization or to the vitroplast formed from vitrinite in coal hydrogenation residues (Mitchell et al., 1977). With an analogous derivation the name, “biocharoplast” can be proposed in this work to denote the material generated from lignocellulosic material losing their integrity during HTC process. The pressure existing in the reactor can be considered responsible for the formation of biocharoplast at relatively low temperature (250 °C), because cell-wall integrity is maintained during torrefaction (or pyrolysis) performed at similar temperature under atmospheric pressure (Pohlmann et al., 2014). A wide distribution of reflectances was observed in the biocharoplast of HTC 250 MS with average values of 0.38% (Fig. 3b and Table 2), which accounts for the major component in the sample. A carbonaceous material maintaining a certain vegetal structure but homogenized cell-walls was also common in the HTC 250 MS. Occasionally, transitions between the structured tissue and biocharoplast were observed (Fig. 2d). The distribution of reflectances of the structured material was narrower than that of biocharoplast (Fig. 3b) and the average values slightly higher (0.42%).

The acid digestion of maize silage caused significant transformation in the parent material, responsible for a different behavior upon hydrothermal carbonization. HTC 230 MSD image in Fig. 2f shows the typical appearance of the digestate residue. Unlike the hydrochars from RMS, hydrochar from digestate showed systematically a granular texture, formed by micrometer sized carbonaceous spheres. The average reflectance of the granular material was intermediate between dark and light textinite formed at the same temperature from RMS and had a relatively narrow distribution of reflectances (Fig. 3c). The acid digestion apparently accelerates the nucleation generating a rather refractory material similar to micrinite in coal that may have difficulties to coalesce.

4. Conclusions

Optical microscopy of hydrochar reveals valuable information about the transformations occurring upon biomass hydrothermal carbonization, which was caused by wall shrinkage and formation of biocharospheres at expenses of the cell-walls at 230 °C and formation of a carbon-enriched homogeneous shapeless mass named biocharoplast at 250 °C. The 20 °C increment of HTC temperature made biomass able to melt forming an optically homogeneous material. Digestate hydrochar at 230 °C had a granular structure indicating an acceleration of the nucleation with the formation of submicrometer size spheres. Hydrochar reflectance increased with carbon content and allows following the transformations under treatments of different severities and describing sample heterogeneity.

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